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MEMORANDUM

MWH
2353 130th Avenue N.E., Suite 200
Bellevue, Washington 98005
Phone: (425) 602-4000
Fax: (425) 867-1970

To: Rick Clegg, IDEQ
Cc: Bob Geddes, P_4 Production, LLC
From: Mark Rettmann, MWH
Bill Wright, MWH

Date: June 1, 2005 **Deleted:** May 27

Reference: P_4 Production Southeast Idaho Mine-Specific Selenium Program

Subject: Chromium Speciation Study in Pond Sediment, Stream Sediment, Stream Riparian Soil, and Waste Rock Dump Soil

Introduction

This technical memorandum documents the results and findings of the chromium speciation study conducted as part of the P_4 Production Southeast Idaho Mine-Specific Selenium Program. This study supports the site investigations (SIs) at P4 Production's Enoch Valley, Henry, and Ballard mines. A Chromium Speciation Sampling Memo, included as Attachment A, was prepared on July 6, 2004, to serve as a work plan/field sampling plan. It documents sampling and laboratory analysis procedures, sampling stations, proposed evaluation, and background regarding the need for this chromium speciation study. The memo was prepared with technical input from the Idaho Department of Environmental Quality and was approved by IDEQ prior to sampling in July 2004.

This study was conducted to determine the local or mine-specific ratio of hexavalent chromium (Cr[VI]) to total chromium in pond and stream sediments, stream riparian soil, and waste rock dump soil. The IDEQ would not allow P4 Production to drop chromium from the analyte list for the SIs based on the interim surface water and sediment data collected in 2002. In IDEQ's comments on P4 Production's Draft SI and EE/CA Work Plans, IDEQ recommeded that site-specific speciation studies be conducted by P4 Production. IDEQ's comment and P4 Production's response as found in the document entitled "Responses to Agency Comments on Draft SI and EE/CA Work Plans" is included below.

> "24. **IDEQ Comment:** Section 3.1.1, Page 3-7, 1st-3rd Para: The Statement of Work contained in Monsanto's executed Administrative Order on Consent specifies the contaminants of concern for the Site Investigations. Monsanto may add other constituents of interest, if so desired, but they are not at liberty to drop or replace the specified analytes, particularly for optimizing laboratory costs. The designate COC list consists of Se, Cd, Cr, Ni V, and Zn for all media except vegetation and regulated surface water, which may exclude Cr, Ni and V. If Monsanto wants to pursue elimination of Chromium from the soil and sediment COC list based on their understanding of the current screening assumptions, they should propose site-specific speciation studies that clearly document the current assumptions used by USEPA and NOAA in establishing their Cr threshold values.

Cr should not be dropped from the COC list until the results of the study are reviewed and approved by the Agencies.

Response: *Accepted with clarification. It appears simpler and more accurate to state that the agencies are willing to drop chromium, nickel, and vanadium in all media except groundwater, soil, and sediment. P_4 Production may specify that these target elements are retained for these three media but may, upon IDEQ approval, be dropped following receipt, review, and approval of appropriate studies or arguments. Specifically, P_4 Production is planning a speciation study for chromium in sediment and soil to document the proportion of the hexavalent species relative to the 14% assumed by USEPA in establishing risk-based benchmarks. P_4 Production will document the plans for this study by means of program memorandum and will be asking for agency input on sampling locations (P_4 Production is looking at biased sampling of areas known or suspected of being chromiferous). P_4 Production is considering risk-based arguments for the deletion of nickel and vanadium in soil. In summary, the three elements mentioned in this comment will be added to the contaminant of potential concern list for groundwater, sediment, and soil pending approval to do otherwise from the agencies."*

Sampling Summary

Chromium speciation sampling was conducted on July 15, 16, and 17 of 2004. A total of fourteen samples were analyzed for total chromium by method 3050/6010 and hexavalent chromium by method 3060/7196. The fourteen samples were collected from the various media at the following locations:

- Three sediment samples collected from ponds (MSP019, MSP055, and MSP059);
- Three sediment samples collected from streams (MST130, MST089, and MST067);
- Three riparian soils collected near streams (MST130, MST089, and MST067);
- Three waste rock soil samples collected from Spring 2001 waste rock dump locations (MWD091-2, MWD086-0, MWD080-6); and,
- Two field QA samples (equipment blank and deionized source water blank).

The three Spring 2001 waste rock dump station locations were located using the Spring 2001 station GPS coordinates. Black shales at the three waste rock dump stations were sampled since the sampling in Spring 2001 was biased towards them and we hypothesized that this form of waste rock would be likely to have the highest mineral content. (Pond sediments, which are primarily run-of-mine waste rock, would be expected to give a more averaged result.) Table 1 below presents the July 2004 station coordinates for this activity.

Table 1

GPS Station Coordinates for Chromium Speciation Sampling			
Station Name	Station	GPS Coordinates[a]	
		Latitude	Longitude
Enoch Valley Mine Bat Cave Pond	MSP019	42 52 23 N	111 24 05 W
Henry Mine South Pit Pond	MSP055	42 51 35 N	111 27 06 W
Ballard Mine Pit #4 Stock Pond	MSP059	42 49 12 N	111 28 53 W
Ballard Creek, headwaters	MST067	42 49 24 N	111 29 36 W
Wooley Valley Creek, below North Fork Wooley Valley Creek	MST089	42 49 29 N	111 26 19 W
Angus Creek, below Angus Creek Reservoir	MST130	42 49 38 N	111 23 58 W
Ballard Mine Pit #1 Overburden Dump #1	MWD080	42 50 00 N	111 29 40 W
Henry Mine Pit #1 Overburden Dump	MWD086	42 52 41 N	111 28 01 W
Enoch Valley Mine South Dump	MWD091	42 51 57 N	111 23 39 W

Notes:
[a] NAD27 datum, reported as (degrees, minutes, seconds)

Sample Results

Table 2 below presents the results of the chromium speciation sampling (total and hexavalent chromium).

Table 2

Total and Hexavalent Chromium in Sediment, Riparian Soil, and Waste Rock Soil (mg/kg-dw)[a]						
Station Name	Station	Matrix, Feature	Total Chromium (EDL, 1.5)	Flag	Hexavalent Chromium (EDL, 0.20)	Flag
Enoch Valley Mine Bat Cave Pond	MSP019	Sediment, Pond	450		-8.1	0.20 UJ
Henry Mine South Pit Pond	MSP055	Sediment, Pond	940		-4.1	0.20 UJ
Ballard Mine Pit #4 Stock Pond	MSP059	Sediment, Pond	870		-14	0.20 UJ
Ballard Creek, headwaters	MST067	Sediment, Stream	320		-35	0.20 UJ
Wooley Valley Creek, below North Fork Wooley Valley Creek	MST089	Sediment, Stream	110		-15	0.20 UJ
Angus Creek, below Angus Creek Reservoir	MST130	Sediment, Stream	100		-9.2	0.20 UJ
Ballard Creek, headwaters	MST067	Riparian Soil, Stream	120		-38	0.20 UJ
Wooley Valley Creek, below North Fork Wooley Valley Creek	MST089	Riparian Soil, Stream	48		-38	0.20 UJ
Angus Creek, below Angus Creek Reservoir	MST130	Riparian Soil, Stream	95		-9.3	0.20 UJ
Ballard Mine Pit #1 Overburden Dump #1	MWD080	Waste Rock Soil, WRD	900		7.3	J
Henry Mine Pit #1 Overburden Dump	MWD086	Waste Rock Soil, WRD	990		-6.3	0.20 UJ
Enoch Valley Mine South Dump	MWD091	Waste Rock Soil, WRD	1100		17	J
Total and Hexavalent Chromium in Quality Assurance Samples (mg/L)						
Angus Creek, below Angus Creek Reservoir	MST130	Water, QA Blank	0.00025	NA	-0.73	NA
Angus Creek, below Angus Creek Reservoir	MST130	Water, QA EQ Blank	0.0012	NA	-0.79	NA

Notes:
[a] All samples were analyzed at the University of Idaho - Analytical Sciences Laboratory, Holm Research Center
WRD - Waste Rock Dump

Flag refers to the USEPA data qualifier (flag) assigned to the data resulting from the data validation procedure. More than one flag may be assigned during the data validation process.

Data qualifier definitions are:

(U) - The material was analyzed for, but was not detected above the level of the associated value. The associated value is 5 X the highest blank concentration, or the sample detection limit.
(J) - The associated value is an estimated quantity.
(R) - The data are unusable.
(UJ) - The material was analyzed for, but was not detected. The associated value is an estimate and may be inaccurate or imprecise.
NA - Not Applicable

Data Evaluation

All hexavalent chromium results were not detected above the laboratory's estimated detection limit of 0.20 mg/kg for all the samples except two of the three waste rock soils. All sediment-pond, sediment-stream, and riparian soil sample were not detected.

The site-specific proportions of Cr(III) and Cr(VI) were determined by medium (i.e., pond sediment, stream sediment, stream riparian soil, and surficial waste rock soil). Riparian soil applies only to stream riparian soils and pond riparian zones are regarded as run-of-mine surficial waste rock, while the surficial waste rock category is specific to black shales (i.e., relatively unweathered, and supposedly highly mineralized, waste shales). For each of the four media, the observed ratios were fit to a 4-parameter lognormal distribution and the 95th percentile of that distribution was calculated. The ratios were assumed to be between -1 and 1. (Because data were not censored, negative results have to be accommodated; these provide a measure of the overall error of the analytical method below the estimated detection limit).

The site-specific total chromium PRGs by medium were then calclulated using the site-specific proportions of Cr(III) and Cr(VI). Because Cr(VI) is far more toxic than Cr(III), the site-specific PRG, in the presence of any Cr(VI), is simply inversely proportional to the fraction of total Cr that is hexavalent (i.e., the lower the proportion of Cr(VI), the higher the PRG). If no Cr(VI) is present, the total Cr PRG obviously defaults to the Cr(III) PRG. The site-specific proportions of Cr(III) to Cr(VI) by medium and the site-specific total chromium PRGs are provided in Table 3 below.

Table 3

Site-specific Adjustments of Total Cr PRG										
Analyte	USEPA-9 PRG, mg/kg dw	USEPA-9-assumed Proportions	Site-specific Proportions* by Medium				Site-specific PRG by Medium, mg/kg dw			
			pond sediment[1]	stream sediment[2]	riparian soil[3,3a]	surficial waste rock[4]	pond sediment	stream sediment	riparian soil	surficial waste rock
total Cr	450						2,800	100,000	100,000	3,400
Cr(III)	100,000	0.86	0.98	1.0	1.0	0.98				
Cr(VI)	64	0.14	0.023	-0.082	-0.067	0.019				

* Upper 95th percentile of the proportion of Cr(VI).

[1] Proportion of Cr(VI) distributed 4-parameter lognormally with a lower bound of -0.019 and an upper bound of 1.0.

[2] Proportion of Cr(VI) distributed 4-parameter lognormally with a lower bound of -0.60 and an upper bound of -0.065.

[3] Proportion of Cr(VI) distributed 4-parameter lognormally with a lower bound of -1.0 and an upper bound of -0.062.

[3a] Applies only to stream riparian zones; pond riparian zones are regarded as run-of-mine surficial waste rock.

[4] Proportion of Cr(VI) distributed 4-parameter lognormally with a lower bound of -1.0 and an upper bound of 0.023.

Conclusions

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Table 3 above summarizes the mine-specific total chromium PRG by medium to be used for the P4 Production Southeast Idaho Mine-Specific Selenium Program.

The hypothesis stated in the Chromium Speciation Sampling Memo, "We believe the fraction of Cr(VI) is closer to 0% than the 14% assumed by EPA Region 9", has been accepted as the result of this mine-specific chromium speciation study. The percentage of hexavent chromium is documented herein to be well less than 3% (at the 95th percentile of the distribution) in all four media.

The mine-specific total chromium PRG was compared to the Interim Surface Water and Sediment Investigation results (sediment and surface water) and the 2004 Site Investigation results (sediment, surface water, and riparian soil). No results exceed the mine-specific PRGs.

Based on the mine-specific percentages of hexavalent chromium, and the fact that no results exceed the mine-specific total chromium PRGs, P4 Production recommends deleting chromium from the list of contaminants of potential concern for all media.

MEMORANDUM

MWH
2353 130th Avenue N.E., Suite 200
Bellevue, Washington 98005
Phone: (425) 602-4000
Fax: (425) 867-1970

To: Rick Clegg, IDEQ
cc: Bob Geddes, P_4 Production, LLC
From: Bill Wright, MWH

Date: July 6, 2004

Reference: P_4 Production Southeast Idaho Mine-Specific Selenium Program (1010076.011601)

Subject: Chromium Speciation Sampling in Sediment, Riparian Soil, and Waste Rock Dump Soil

Introduction

The purpose of this memorandum is to document the stations and media to be sampled for chromium speciation in 2004 as part of the P_4 Production Southeast Idaho Mine-Specific Selenium Program. This memorandum has been prepared with input from IDEQ. This activity supports the site investigations at P_4 Production's Enoch Valley, Henry, and Ballard mines. This activity, chromium speciation, is being conducted to determine the local or mine-specific ratio of hexavalent chromium (Cr[VI]) to total chromium in sediment, riparian soil, and waste rock dump soil.

Background

The reason determining the ratio of Cr(VI) is important is because the preliminary risk-based benchmark being used by the regulatory agency for chromium is the Region 9 Preliminary Remedial Goal (PRG) for total chromium. This preliminary benchmark assumes, unrealistically, that one-seventh (approximately 14%) of the chromium is present in the far more toxic hexavalent state. Trivalent chromium, the typical form found in the environment, is virtually non-toxic; in fact, it is a mineral widely used in high doses as a nutritional supplement. Trivalent chromium occurs naturally in rocks, soil, plants, animals, and volcanic emissions. This form is believed by many to play a nutritional or pharmaceutical role in the body, but its mechanism of action is unknown.

Hexavalent chromium is produced industrially when trivalent chromium (Cr[III]) is heated in the presence of mineral bases and atmospheric oxygen (for instance, during metal finishing processes). It is this form of chromium that has proven to be of the greatest occupational and environmental health concern. Hexavalent chromium is unstable under environmental conditions and is encountered as a contaminant under conditions where large quantities of the hexavalent form is used in an industrial process or when trivalent chromium is converted to hexavalent chromium under industrial processes.

It is for the above reasons, and the fact that there are no industrial processes using chromium at the mines under consideration, that the PRG assumed ratio is unrealistic. We believe the fraction of Cr(VI) is closer to 0% than the 14% assumed by EPA Region 9. The purpose of this

activity is to establish the actual mine-specific ratio of hexavalent chromium to total chromium in sediment, riparian soil, and waste rock dump soil. Chromium in other environmental media is not of concern.

Sediment

Historical total chromium results in sediment for stations relating to P_4 Production's mines were reveiwed. One pond station from each of the three mines (i.e., three total ponds stations) and three stream stations, with the highest total chromium concentrations during the May 2002 interim surface water and sediment sampling event, were chosen for chromium speciation sampling for sediment.

The three pond stations (i.e., one station from each mine) with the highest total chromium in sediment are as follows:

- MSP059 (Ballard Mine Pit #4 Stock Pond) at 700 mg/kg dw,
- MSP055 (Henry Mine South Pit Pond) at 610 mg/kg dw, and
- MSP019 (Enoch Valley Mine Bat Cave Pond) at 580 mg/kg dw.

The three stream stations with the highest total chromium in sediment are as follows:

- MST130 (Angus Creek, below Angus Creek Reservoir) at 78 mg/kg dw,
- MST089 (Wooley Valley Creek, below North Fork Wooley Valley Creek) at 76 mg/kg dw, and
- MST067 (Ballard Creek, headwaters) at 76 mg/kg dw.

Riparian Soil

No historical chromium data for riparian soil exists for the P_4 Production mines. Therefore, riparian soil sampling will occur at the three stream stations that exhibited the highest total chromium in sediment and are listed above. One randomly selected composite soil sample will be collected at each location.

Waste Rock Dump Soil

Historical chromium data from waste rock dump soil sampling in Spring 2001 was reviewed. Black-shales on waste rock dumps will be sampled since the sampling in Spring 2001 was biased towards them. One black-shale sample will be collected from a waste rock dump at each of the three P_4 Production mines (i.e., three waste rock dump soil samples will be collected). One waste rock dump location from each mine with the highest concentration of total chromium will be sampled.

The three Spring 2001 waste rock dump stations (i.e., one station from each mine) with the highest total chromium in black shale soils are as follows:

- MWD091-2 (Enoch Valley Mine South Dump) at 1,400 mg/kg dw,
- MWD086-0 (Henry Mine Pit #1 Overburden Dump) at 1,100 mg/kg dw, and
- MWD080-6 (Ballard Mine Pit #1 Overburden Dump #1) at 1,100 mg/kg dw.

The stream and pond sampling stations and the waste rock dump locations specified above can be found on Figure 2-1, "Program Sampling Locations," of the SAP.

Sampling and Analysis Procedures

Sampling procedures for this activity will be in accordance with the P_4 Production Southeast Idaho Mine-Specific Selenium Program, sampling and analysis plan (SAP), project work plans (PjtWPs), and project field sampling plans (PjtFSPs) supporting the site investigations (published 2004). Specifically, sampling procedures are detailed in the program Quality Assurance Plan (PgmQAP) of the SAP and relevant standard operating procedures (SOPs). Sediment sampling procedures are detailed in Section 6.2.6 of the PgmQAP and SOP-NW-9.3, "Collection of Sediment Samples", riparian soil sampling procedures are detailed in Section 6.4.1 of the PgmQAP and SOP-NW-7.2, "Collection of Soil Samples", and waste rock dump soil sampling procedures will be consistent with the procedures followed for the Spring 2001Area-Wide Investigation waste rock dump soil (i.e., black shales) sampling and SOP-NW-7.2, "Collection of Soil Samples". The procedure for the Spring 2001Area-Wide Investigation waste rock dump soil sampling included locating an area of exposed black-shales upon a waste rock dump, obtaining GPS coordinates, digging an approximately 1-ft deep hole and obtaining the sample by scraping the face of the hole. No sieving in the field was performed.

The pond and stream sediment samples, the riparian soil samples, and the waste rock dump soil (i.e., black shales) samples will be analyzed at the University of Idaho, Holm Research Center, for total chromium by ICP (EPA 3050/6010) with a method detection limit (MDL) of 0.38 mg/kg dw and hexavalent chromium by alkaline digest & colorimetric analysis (EPA 3060/7196) with a MDL of approximately 0.10 mg/kg dw.

Data Evaluation

The mean percent hexavalent chromium and confidence and tolerance bounds will be calculated by medium. The mine-specific ratio of hexavalent chromium to total chromium in sediment, riparian soil, and waste rock dump soil will be determined from these results. This activity assumes that the fraction of hexavalent chromium is variable but in a way that is not dependent on the total chromium concentrations. In other words, locations with high concentrations of total chromium are being targeted in anticipation of seeing very low amounts of hexavalent chromium.

The sample results, and findings from this activity (i.e., mine-specific chromium ratio) will be reported in the SI report. If the results are as predicted, P_4 Production may use them as a basis for deleting chromium from the list of contaminants of potential concern.